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**The Photolysis of Bis(cyclopentadienyl)molybdenum Oxide in
Water. The Catalytic Production of Hydrogen.**

by

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J.I. Zink, and W.C. Kaska**

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**The Photolysis of Bis(cyclopentadienyl)molybdenum Oxide in Water. The
Catalytic Production of Hydrogen****

By Robert J. Flesher*, Colin Creaser[≠], Vojislav I. Srdanov*, Galen D. Stucky*, Jeffrey
I. Zink* William C. Kaska*

Photocatalytic production of hydrogen from water has been a long term goal of inorganic photochemistry^[1a-z]. Previous research efforts can be summarized in terms of four methods that will decompose water into hydrogen and oxygen. They include the use of simple metal salts^[1a,d,h], metal complexes^[1a,b,m], intermolecular electron transfer with sensitizers^[1a,z], and photoelectrochemical^[1u] methods.

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University of Tübingen, are greatly appreciated.

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Early studies centered around intermolecular electron transfer with sensitizers^[1a] although catalytic cycles were difficult to complete because sacrificial agents had to be used to maintain the reaction. The recent application of photoelectrochemical methods offers considerable promise, especially with photosensitive dye containing cells^[1u]. Complementary use of metal complexes,^[1z] however, appears to be particularly effective for two reasons a) many metal complexes can photocatalyze the decomposition of water and b) ligand design offers the potential of modifying metal complexes to achieve catalysis. Nevertheless there are few well characterized metal complexes that will photochemically produce hydrogen from water^[1s]. We report here the photocatalytic synthesis of hydrogen and peroxide from water by bis(cyclopentadienyl)molybdenum oxide.^[2a,b]

Continuous irradiation of $(C_5H_5)_2Mo=O$ in water with a 450 W medium mercury pressure lamp gives hydrogen gas and peroxide. No oxygen gas can be detected during the photolysis^[3] which is very unusual since irradiation of the complex in strictly organic solvents gives considerable oxygen gas.^[2a]

The mole ratio of hydrogen produced during photolysis to $Cp_2Mo=O$ is greater than one, hence the molybdenum system behaves as a catalyst. A T.O. of approximately 2 is observed after 81 hr of photolysis or T.O./hr = 0.02. During the photolysis, a brown red solid, $[Cp_2Mo(O)_2Mo(O)_2]_2$,^[4] slowly deposits, which was identified by infrared comparison with an authentic sample. When the deposited solid was separated from the original photolysis solution, washed with freshly degassed water and re-suspended in degassed water, hydrogen production continued at a reduced rate. An authentic sample suspended in water did not produce hydrogen gas, however. In order to trace the oxygen atom presence, the photolysis of $Cp_2Mo=O$ in 95% $H_2^{18}O$ was studied. Collection of the gas above the reaction mixture after 4 hr of photolysis with a 1000 W mercury lamp showed only the presence of hydrogen. No $^{18}O_2$ above the background was detected in the mass spectrometer.^[5] This suggests that H^+ is reduced to H in the photolysis process and the oxygen atom in water is oxidized from

the -2 state to the -1 state. Thus hydrogen appears as H_2 gas and oxygen as H_2O_2 or OOH^\cdot .^[6,7,8] Photolysis of specific polyoxomolybdates and tungstates can generate species that will give peroxide.^[9] Evidently the peroxide species slowly degrades the catalyst. To test this hypothesis, Me_3P was added to the photolysis mixture to scavenge the peroxide and thus prevent destruction of the $Cp_2Mo=O.H_2O$.^[2a] Photolysis proceeded for 12 hr with a total production of 90 μ moles of hydrogen from 45 μ moles of catalyst with a T.O. of 2 and a T.O./hr of 0.16 which is ten times the previous result with out the addition of Me_3P . The $Me_3P=O$ formed was identified by ^{31}P NMR and 1H NMR spectroscopy.^[10] The following diagram depicts the essential parts of the reaction,

insert Scheme 1

- [1] a) D. J. Cole-Hamilton, D.W. Bruce, in Comprehensive Coordination Chemistry, (Ed. G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon Press, 1987, 6, p.487, and references therein. This is a description of water splitting; b) U. Kolle, M. Gratzel, Angew. Chem. Int. Ed. Engl. 1987, 26, 567; c) T. Ymase, T. Kawa, Inorg. Chem. Acta. 1980, 45, L 55; d) S. Leutwyler, E. Schumacher, Chimia, 1977, 31, 475; e) A. Harriman, J. Chem. Soc. Faraday Trans. 2 1986, 2267; f) P. A. Jacobs, J. B. Uytterhoevan, H.B. Beyer, J. Chem. Soc. Chem. Comm. 1977, 128; g) A. Harriman, G. Porter, J. Chem. Soc. Faraday Trans. 2 1982, 78, 1937; h) K. Tennakone, A. H. Jayatissa, W. Wijerantne, J. Chem. Soc. Chem. Comm. 1988, 497; i) K. Sayama, A. Tanaka, K. Domen, K. Maruya, T. Ohishi, J. Phys. Chem. 1991, 95, 1345; j) G. Gard, T. L. Brown, J. Am. Chem. Soc. 1982, 104, 6340; k) G. Calzaferri, L. Forss, W. Sphani, Chemie in Unser Zeit, 1987, 21, 161; l) J. R. Darwent, M. D. Douglas, A. Harriman, G. Porter, M-C Richaux, Coord. Chem., Rev., 1982, 44, 83; m) L. Salsini, M. Pasquali, M. Zandomenighi, C. Festa, P. Leoni, D. Braga, P. Sabatino, J. Chem. Soc. Dalton Trans. 1990, 2007; n) J. M. Lehn, J.P. Sauvage, R. Zissel, Nouveau J. de Chemie, 1980, 4, 355; o) K. Sakai, K. Matsumoto, J. Mol. Catalysis 1990, 62, 1, and references therein; p) E.

- Vrachnou, C. Mitsopoulou, D. Katakis, J. Konstantatos, in Photoconversion Processes for Energy and Chemicals, 1990 (Ed. D. O. Hall, G. Grass), Elsevier, N. Y. ;q) D. J. Cole-Hamilton, R. F. Jones, J. R. Fisher, D. M. Bruce in Photogeneration of Hydrogen, (Ed. A. Harriman, M. A. West), Academic Press, 1982, London p.105; r) J. Kiwi, K. Kalyanasundaram, M. Gratzel, Structure and Bonding, 1982, 49, 37; s) P. R. Ryason in Survey of Progress in Chemistry 1980, 9, 89, (Ed. A. F. Scott), Academic Press N. York 1980. t) H. Parlar, W. Schumann, Nachr. Chem. Tech. Lab. 1988, 36, 1101, u) M. Kaneko, A. Yamada, Adv. in Polymer Sci. 1984, 55, 1, Springer Verlag, 1984; v) B. O'Regan, M. Gratzel, Nature, 1991, 353, 737; w) A. Harriman, Platinum Metal Review, 1983, 27, 102; x) P. Keller, A. Moradpour, E. Amouyal, H. B. Kagan, Nouv. J. de Chemie, 1980, 4, 377; y) V. N. Parmon, K. I. Zamareav, in Photocatalysis, Fundamentals and Applications, (Ed. N. Serponi, E. Pelizzette); John Wiley and Sons, 1988, P.565; z) P. C. Ford, A. F. Friedman, in Photolysis, Fundamentals and Applications, (Ed. N. Serponi and E. Pelizzetti), John Wiley & Sons, 1988 p. 541; V. Balzani, F. Barigelletti, L. de Cola, Topics in Current Chemistry 1990, 158, 32; V. Balzani, L. Moggi, M.F. Manfrin, F. Bolletta, M. Gleria, Science, 1975, 189, 852.
- [2] a) N. D. Silawe, M.Y. Chiang, D. R. Tyler, Inorg. Chem. 1985, 24, 4219; Photolysis of $\text{Cp}_2\text{Mo=O}$ in organic solvents with various phosphines gives no $\text{R}_3\text{P=O}$; b) N. D. Silawe, M. R. M. Bruce, C. E. Philbin, D. R. Tyler, Inorg. Chem. 1988, 27, 4669; c) M. L. H. Green, A. H. Lynch, M. G. Swanwick, J. Chem.Soc. Dalton Trans. 1972, 1445.
- [3] The mass spectra were measured with a fabricated quadruple mass spectrometer which used an Auxum monitoring system. Most mass spectrometers have a high $m/e=2$ background. Hence only measurements with internal standards are reliable measurements of H_2 , or He. The measured m/e ratios were extrapolated to zero time of sample because of the large discrimination introduced by preferential

pumping of H_2 under molecular flow^[7]

[4] G. J. S. Adam, M. L. H. Green, J. Organomet. Chem. 1981, 208, 299.

[5] Reactions performed in D_2O showed only D_2 gas. In order to trace the oxygen atom an IR analysis was made of the red-brown solid which precipitated during the photolysis. The material prepared according to the literature^[4] and the material collected from the photolysis compared exactly by infrared. The sample prepared in $H_2^{18}O$ showed ν Mo=O bonds at 701 735, 611, 641 compared to 913 and 868 cm^{-1} . This suggests that the oxygen atom may remain attached to the molybdenum during the photolysis and cause catalyst degradation.

[6] a) E. Papaconstantinou, Chem. Soc. Rev., 1989, 18, 1; b) T. Yamase, Inorganica Chimica Acta, 1981, 54, L165; c) *ibid*; 1982, 64, L155; d) B. Kraut, G. Ferraudi, J. Chem. Soc. Dalton Trans. 1991, 2063.

[7] S. Leutwyler, E. Schumacher, Chimia 1977, 31, 475.

[8] The exact nature of $Cp_2Mo=O$ in water is not clear, although it may well be as $Cp_2Mo(OH)^+OH^-$ since the pH of the compound in water is 9. Previous work has shown that Cp_2MoCl_2 undergoes rapid chloride aquation in water with no $M-C_5H_5$ protonolysis over weeks at pH 7.6^[9]

[9] L. Y. Kuo, M. G. Kanatzidis, T. J. Marks, J. Am. Chem. Soc., 1987, 109, 57

[10] The presence of hydrogen peroxide or metal peroxo species in water photolysis is known^[12,13,14]

[11] The ^{31}P chemical shift of $Me_3P=O$ was observed at +55.1 ppm in the D_2O sample. An authentic sample of Me_3P in D_2O showed a resonance at δ -62. ^[15] When O_2 was introduced and the sample allowed to stand, the δ -62 peak disappeared and a peak at δ +55.1 appeared. ^[16] In organic solvents the δ of $Me_3P=O$ is 36.2 and in MeOH it is at + 45.4 ppm. The chemical shift of Me_3P in D_2O with a trace of H_2O_2 showed a peak at δ + 55.1.

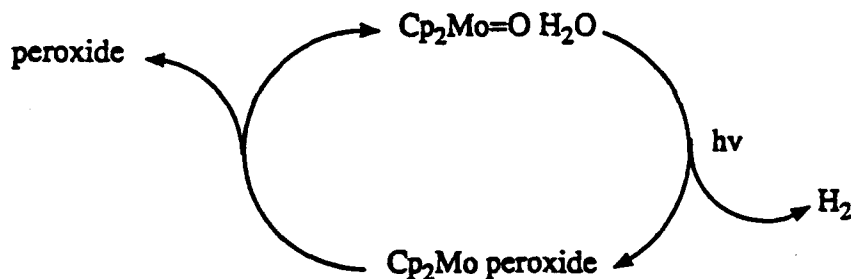
[12] a) K. Kalyanasundaram, M. Gratzel, E. Pellizzetti, Coord. Chem. Rev. 1986, 69, 57;

- [13] J. E. Guillet, Pure and Applied Chem. 1991, 63 917
- [14] T. Shinoda, J. Mol. Catalysis, 1991, 64, 1.
- [15] Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis, (Ed. J. G. Verkade, L. D. Quin), 1987 VCH, Inc. Florida, USA.
- [16] F. Seel, H. J. Bassler, Z. Anorg. Allg. Chemie 1976, 423, 67.
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Experimental Procedure. A pale pink water (D_2O) solution (degassed) four times by freeze thaw methods before photolysis) of $Cp_2Mo=O$, 45 μ moles, was photolyzed for a total of 81 hr by placing the sample in an evacuated quartz tube in the beam of a 450 W Medium pressure mercury lamp. A total of 69.53 μ moles of hydrogen gas was collected from the reaction system by Toepler pumping every four hr. The reaction vessel was cooled in liquid nitrogen and the evolved gas was passed through a liquid nitrogen cooled trap. The gas was measured three times in a calibrated volume at three different pressures to check for homogeneity. An average of the three values was used in calculating the total amount of gas evolved. The turn over frequency of 1.54 or approximately 2 with a T.O./hr of 0.02 is observed. Blank experiments of $Cp_2Mo=O$ in D_2O without photolysis gave no D_2 gas. D_2O without the presence of $Cp_2Mo=O$ also gave no D_2 gas after photolysis.

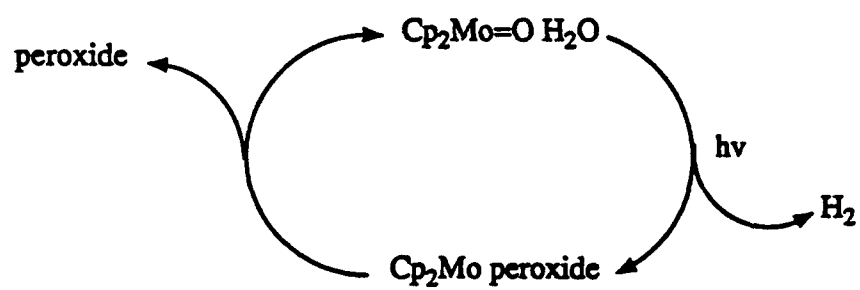
**Reason for Submitting this report as a Rapid Communication to
Angewandte Chemie**

Oil and coal have been the most dominant fuels for society for more than a century and a half. Both of these materials have their limitations in terms of decreasing availability and environmental concerns. In recent years, the ability to handle and use hydrogen as a fuel has increased greatly. What remains is to find a cheap reliable source for hydrogen from the abundant raw material, water. Inorganic photocatalysis with transition metal complexes has been a major focus of research for making new materials that will accelerate the generation of hydrogen from water. In this paper we



Scheme 1

report an instance where catalytic synthesis of hydrogen from water with the assistance of a well defined organometallic complex with no sacrificial donors. Only one metal atom is used for the formation of hydrogen and peroxide. Very few well defined single molecular systems are known to photolytically effect the cleavage of water. This special molecular oxide which photochemically releases oxygen in organic solvents and then changes its behavior by releasing hydrogen in water is a system that warrants further development. As such it represents an instance of general technical interest. Therefore we submit it for consideration as a publication in Angewandte Chemie.



Scheme 1

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